

PATENT SPECIFICATION

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NO DRAWINGS



1 220 384

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(31) Convention Application Nos.

F 51877 IVd/39c (32) Filed 20 March 1967

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C3P 2D1A 2D8 2K7 2K8 2K9 2P1B 2P1C 2P1E5 2P1F
2P2A4 2P2C 2P4A 2P4C 2P6A 2P6G 2T1A 7D2A1
7D8 7K2 7K8 7P1B 7P1C 7P1E5 7P1F 7P2A4
7P2C 7P4A 7P4C 7P6A 7P6G 7T1A 8D1B 8D3A
8D3B 8D8 8K2 8K8 8K9 8P1B 8P1C 8P1E5 8P1F
8P2A4 8P2C 8P4A 8P4C 8P6A 8P6G 8T1A 9D1C
9D8 9K2 9K8 9P1B 9P1C 9P1E5 9P1F 9P2A4 9P2C
9P4A PP4C 9P 6A 9P6G 9T1A

(54) SYNTHETIC RUBBER LATICES

(71) We, **FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT**, of 509, Leverkusen, Germany, a corporate body organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to synthetic rubber latices.

Shaped articles and in particular hollow bodies of natural or synthetic polymers, elastomers in particular, are often produced by the dip-tank process in which a mould, for example, made of wood, glass, porcelain, metal or plastics is first dipped into a bath containing a coagulation solution and then into an emulsion of an elastomer. A polymer film is formed on the surface of the mould as the coagulant adhering to the surface of the mould destroys the emulsion. This film may be of course subsequently removed from the mould. This process is also known as the coagulant process. The coagulation solution is known as the coagulant bath and the polymer emulsion as the latex bath.

The success of this process is governed very largely by the nature and composition of the coagulant and latex baths. Film thickness and surface quality can be influenced in dependence upon the types of baths used. The deposited film can also be thickened by repeating the procedure. The described process has already been carried out with natural rubber latices, polychloroprene latices and latices of butadiene-acrylonitrile copolymers.

In the case of the butadiene-acrylonitrile

copolymers, the results of the process have never been satisfactory because a poor, generally non-coherent film is formed whose surface quality is entirely unsatisfactory.

This invention relates to a copolymer latex that is suitable for use in the dip-tank process. The invention provides a copolymer latex containing in emulsified form a copolymer of from 40 to 98 parts by weight of a conjugated diene, 0.1 to 50 parts by weight of at least one monoolefinically unsaturated comonomer, 0.1 to 10 parts by weight of an olefinically unsaturated carboxylic acid having 3 to 6 carbon atoms and 0.1 to 10 parts by weight of a long chain carboxylic acid having 10 to 30 carbon atoms or a mixture of such acids.

The invention also covers a process for producing a copolymer latex which comprises emulsifying a mixture of (a) 40 to 98 parts by weight of a conjugated diene, (b) 0.1 to 50 parts by weight of at least one monoolefinically unsaturated comonomer, (c) 0.1 to 10 parts by weight of an olefinically unsaturated carboxylic acid having 3 to 6 carbon atoms and (d) 0.1 to 10 parts by weight of a long chain carboxylic acid having 10 to 30 carbon atoms in an aqueous medium, at a pH below 7 and polymerising the mixture in the presence of a free radical-forming catalyst and an emulsifier at a temperature in the range of from 5 to 100°C.

Completely coherent films of satisfactory thickness and surface quality are obtained on the moulds with this latex by the coagulant process referred to earlier on.

Polymerisation is carried out at a pH value of below 7. For this reason, the long-chain fatty acids added do not act as emul-

sifiers during polymerisation. Their function is to influence polymer deposition during coagulation on immersion of the mould. Nearly insoluble metal salts of these carboxylic acids are formed which have a favourable effect both on the coagulation process and on syneresis.

Polymerisation is continued to a conversion of at least 70% but not more than 95% at a temperature of from 5 to 100°C., preferably between 20 and 60°C., and at a pH value of between just below 7 and 1.

Conjugated dienes containing from 4 to 8 carbon atoms are particularly suitable, the following being mentioned as examples: 1,3-butadiene isoprene, chloroprene, 2,3-dimethyl-1,3-butadiene and 2,3-dichloro-1,3-butadiene.

Monoolefinically unsaturated compounds suitable for use in the process according to the invention include, in particular, derivatives of alkenes with from 3 to 10 carbon atoms and aromatic vinyl compounds, the following being mentioned by way of example: acrylonitrile, methacrylonitrile, methylene glutarodinitrile, ethyl acrylate, butyl acrylate, ethylhexylacrylate, ethyl methacrylate, methyl methacrylate, *n*-butyl methacrylate, glycidyl methacrylate, α -chloroacrylonitrile, acrylamide, vinylisobutylether, vinyl acetate, vinyl chloride, vinylidene chloride, methylvinyl ketone, styrene, 2-vinylpyridine, 9-vinylcarbazole and α -methylstyrene. Unsaturated carboxylic acids suitable for use in the process according to the invention include aliphatic carboxylic acids having terminal olefinic unsaturation and containing from 3 to 6 carbon atoms, e.g. acrylic acid or methacrylic acid.

Carboxylic acids with from 10 to 30 and preferably with from 12 to 18 carbon atoms are employed as the long-chain carboxylic acids used either individually or in admixture. Examples of these acids include saturated and unsaturated acids such as lauric acid, palmitic acid, stearic acid, coconut fatty acid and resinic acids. Oleic acid, linoleic and linolenic acid are mentioned as examples of unsaturated, long-chain carboxylic acids.

Polymerisation is carried out in an aqueous emulsion containing at least one anionic emulsifiers either alone or together with one or more non-ionic emulsifiers. The anionic emulsifiers may be water-soluble or monomer-soluble emulsifiers. Salts of organic sulphuric acid esters, alkane sulphonic acids, alkyl aromatic sulphonic acids and carboxylic acids are used as anionic emulsifiers. Typical representatives include sodium salts of lauryl sulphate, C_{14} -paraffin sulphonates and alkyl-naphthalene sulphonates. The anionic emulsifiers is used in a quantity of between 0.5 and 10% based on the weight of

the monomer mixture. The non-ionic emulsifiers consist of a hydrophobic hydrocarbon and a hydrophilic polyether component. The polyether component consists of from 5 to 50 ethylene oxide units and a terminal hydroxyl group. Typical representatives include stearyl alcohols with 20 ethylene oxide units and nonyl phenols with 20 ethylene oxide units.

The quantities in which the non-ionic emulsifier is used may be between 0.1 and 10% by weight, based on the monomer mixture.

The catalyst system which contains an initiator forming free radicals or which develops free radicals may be effectively used to catalyse polymerisation in emulsion. Dissociable initiators include, for example, peroxide initiators such as hydrogen peroxide, benzoyl peroxide and tert-butyl hydroperoxide and azo compounds such as azo-bis-isobutyronitrile.

The preferred catalyst system is a Redox system by which polymerisation can be favourably directed and which is effective at a low temperature. In the Redox system, the oxidising catalyst component is a water-soluble or partially water-soluble hydroperoxide or persulphate. This component decomposes in contact with a reducing agent such as bivalent iron, sodium hydrogen sulphite, sulphonic acid derivatives or organic amines. The reaction is controlled by keeping the temperature below the point at which the peroxide or persulphate is thermally decomposed, and by effecting the decomposition as desired by adding the reducing agent.

In batch operation, the long-chain carboxylic acids are dissolved in one of the monomers and the resulting solution is introduced into the water/emulsifier system containing the residual monomers.

A chain regulator may be added to the mixture in order to adjust the required molecular weight of the polymer. Aliphatic mercaptans or dithioxanthogenates, for example, may be used as regulators in quantities of from 0.01 to 5% by weight.

Polymerisation is initiated by adding the activator and heating the mixture to the required reaction temperature. The polymerisation temperature is kept constant by cooling. Regulators, activators and emulsifiers may be added to the reaction mixture during polymerisation.

Polymerisation can be terminated at a certain conversion rate by the addition of terminators. They arrest the free radicals present and hence inactivate the catalyst. Suitable compounds include water-soluble reducing agents such as sodium hydrogen sulphite, sodium dithionite, "Rongalite" (trade mark), hydroxylamine, hydrazine and sodium dimethyl dithiocarbamate.

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- Shaped articles and in particular hollow bodies of natural or synthetic polymers, elastomers in particular, are often produced by the dip-tank process in which a mould, for example, made of wood, glass, porcelain, metal or plastics is first dipped into a bath containing a coagulation solution and then into an emulsion of an elastomer. A polymer film is formed on the surface of the mould as the coagulant adhering to the surface of the mould destroys the emulsion. This film may be of course subsequently removed from the mould. This process is also known as the coagulant process. The coagulation solution is known as the coagulant bath and the polymer emulsion as the latex bath.
- The success of this process is governed very largely by the nature and composition of the coagulant and latex baths. Film thickness and surface quality can be influenced in dependence upon the types of baths used. The deposited film can also be thickened by repeating the procedure. The described process has already been carried out with natural rubber latices, polychloroprene latices and latices of butadiene-acrylonitrile copolymers.
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Polymerisation can be terminated at a certain conversion rate by the addition of terminators. They arrest the free radicals present and hence inactivate the catalyst. Suitable compounds include water-soluble reducing agents such as sodium hydrogen sulphite, sodium dithionite, "Rongalite" (trade mark), hydroxylamine, hydrazine and sodium dimethyl dithiocarbamate.

Copolymers of conjugated dienes oxidise fairly readily on account of the residual reactive double bonds resulting in undesired degradation. To prevent degradation, stabilisers or antioxidants are added to the latex either during or after polymerisation. The stabilisers or antioxidants are preferably added in the form of an aqueous dispersion. Latices produced in this process have a solids content which is preferably between about 10 and 40% or even higher. By a creaming process, the solids content may be raised to as high as 60% by weight.

Amine and phenol derivatives are suitable stabilisers.

From the copolymer latices obtained in accordance with the invention so-called dipped products may be produced in a variety of shapes, with sufficient thickness and smooth surfaces, within relatively short immersion periods.

Before the actual dipping operation, the polymer latex is charged with certain additives which enable the polymer to be subsequently vulcanised. Since the polymer contains carboxyl groups, vulcanisation can be effected by adding zinc oxide. Other suitable vulcanising agents include sulphur, orthotolyl biguanide, *p*-quinone dioxime, *N*-cyclohexylethylammonium cyclohexyl ethyl dithio-carbamate, zinc *N*-pentamethylene dithiocarbamate, zinc mercaptobenzthiazole, tetraethyl thiuram disulphide, melamine resins, dimethyl-diphenyl thiuram disulphide, hexamethylene tetramine and sulphenamides. The vulcanising agents are usually added to the latices in the form of aqueous solutions or suspensions. They are used in quantities of from 0.1 to 5% by weight, based on the solids content of the latex. Vulcanisation is carried out at temperatures of from 50 to 150°C. for about 10 to 60 minutes.

Protective colloids may be used in order to obtain a latex stability which is sufficient for the incorporation of the components but is not too high to prevent adequate coagulation.

Styrene/maleic ester copolymers, casein or cellulose derivatives are suitable as protective colloids.

In order to obtain a smooth polymer film over the dip moulds, it is of advantage *inter alia* to use a latex with a high solids content, as less water has to be removed during drying which in turn leads to a reduction in the shrinkage of the wet film. At the same time, a high solids content produces syneresis, *i.e.* the exuding of water. In order to obtain polymer latices of sufficiently high solids content, emulsion polymerisation may be carried out in the presence of a suitably small quantity of water. On the other hand, a low solids content latex may be creamed, providing a high solids

content latex and a serum. The sodium and ammonium salts of alginates are suitable as creaming agents.

The viscosity of the polymer latex has some effect and is determined, *e.g.*, by the solids content, the nature of the protective colloid and the pH-value at which dipping is carried out. The viscosity decreases with increasing pH-value so that by varying the pH value the viscosity may be adjusted. The viscosity of the dip mixture is strongly influenced by the protective colloid which may also act as a thickening agent.

Metal salts are used as coagulants in the coagulant bath. The best results are obtained by using bivalent metal ions (calcium nitrate, calcium chloride), trivalent metal ions generally causing over-rapid coagulation. Ethanol isopropanol, methanol, acetone and water are used as the solvents.

The invention is illustrated by the following examples.

Example 1

A) The following components are introduced into a 40-litre capacity autoclave which is equipped with a stirring mechanism, a thermometer and inlets and which is connected to a cooling system:

10.6 litres of desalted water, 250 g. of a mixture of sodium alkyl sulphonates with an average of 14 carbon atoms in the alkyl group and 444 g. of a 90% pure methacrylic acid.

A solution containing 600 g. of a mixture of long-chain fatty acids with from 12 to 18 carbon atoms, in solution in 3150 g. of acrylonitrile, is then added. This is followed by the addition of 8 g. of diisopropyl xanthogen disulphide, after which the reaction vessel is rinsed with nitrogen. 6000 g. of butadiene are then introduced under pressure and the contents of the autoclave are heated to 35°C.

Polymerisation is initiated with a catalyst system containing the following components: 2 g. of potassium persulphate, 10 g. of the sodium salt of an alkyl sulphonic acid with an average of 14 carbon atoms in the alkyl radical and 400 g. of water as a solvent.

Samples are taken at 30-minute intervals and their emulsified polymer content is determined. This is done by coagulating the latex with methanol and determining the quantity of polymer. When the latex has a solids content of from 6% to 10%, a solution in which 20 g. of diisopropyl xanthogen disulphide are dissolved in 200 g. of acrylonitrile is added thereto. The above-mentioned catalyst solution is then added in each case. When the latex has a concentration of from 15 to 25%, an emulsion containing the following components is added thereto: 4000 g. of a 5% aqueous

5 solution of the sodium salt of diisobutyl naphthalene sulphonie acid, 1 g. of potassium persulphate and 5 g. of the sodium salt of an alkyl sulphonic acid with an average of 14 carbon atoms in the alkyl radical.

10 After a latex concentration of 30% has been reached, polymerisation is terminated by the addition of a terminator solution containing the following components: 75 g. of sodium dithionite, 5 g. of the sodium salt of ethylene diamine tetra-acetic acid and 750 g. of desalted water.

15 The latex is degasified for 3 hours at 40°C. *in vacuo* in order to remove the residual monomers therefrom, and then has added thereto a mixture of styrenised xyleneol and a diphenylamine for the purpose of stabilisation.

20 The latex is adjusted to a pH value of 6 by the addition of dilute ammonia water. 27 kg. of an approximately 30% latex are obtained.

B) The latex then has added thereto a

25 solution of 38 g. of sodium alginate in 4.5 litres of desalted water. After creaming has taken place, which takes about two days, the thick latex with a concentration of from 45 to 50% solids content is separated from the serum.

30 C) The thick latex then has added thereto a mixture (b) containing vulcanising agents, pigments and fillers.

a) 200 parts by weight of a polymer latex (50%) according to Example 1A;

35 b) 2.5 parts by weight of zinc oxide, 1.5 parts by weight of colloidal sulphur, 0.8 part by weight of the zinc salt of dimethyldithiocarbamic acid, 4.0 parts by weight of titanium dioxide and 13.2 parts by weight of a 5% aqueous solution of the sodium salt of a condensation product of naphthalene sulphonic acid and formaldehyde.

40 A pH value of between 9 and 10 is adjusted in the dipping mixture by the addition of approximately 5 parts by weight of an aqueous 5% ammonia solution.

TABLE 1

50	Example	pH value of the mixture	Film thickness in mm. after dipping for		Appearance of the film	Surface of the film.
			1 min.	5 min.		
	2	7.6	0.44	0.66	good	smooth
		8.9	0.27	0.47	very good	smooth
55	3	7.7	0.31	0.44	good	smooth
		8.9	0.26	0.45	very good	smooth
	4	7.7	0.30	0.49	good	smooth
		8.9	0.24	0.43	good	smooth
	5	7.7	0.33	0.57	good	smooth
		8.9	0.28	0.57	good	smooth
60	8	6.8	0.22	0.4	irregular	smooth
		9.0	0.25	0.48	good	

65 A solution containing the following components is used as the coagulant solution: 20 g. of calcium nitrate, 10 g. of calcium chloride, 55 g. methanol and 25 g. of acetone.

70 For dipping by the coagulant process, a dip mould is first of all immersed in the coagulant solution and then in the latex mixture containing the vulcanising agents. Table 1 shows the film thicknesses in dependence upon the residence time and the pH value of the mixture.

75 After dipping, the coated objects are vulcanised in an oven for different periods at temperatures of from 50 to 150°C.

Example 2

Components and procedure as in Example

1, except that the quantity of diisopropyl xanthogen disulphide added amounts to 30 g. at 6% and 10% solids content.

Example 3

85 Components and procedure as in Example 1, except that the quantity of diisopropyl xanthogen disulphide added amounts to 40 g. for solids contents of 6% and 10%.

Example 4

90 Components and procedure as in Example 1, except that the quantity of diisopropyl xanthogen disulphide added amounts to 50 g. for solids contents of 6% and 10%.

Example 5

95 Components and procedures as in Example 1, except that the quantity of diisopropyl xanthogen disulphide added amounts

to 60 g. for solids contents of 6% and 10%.

Example 6

- 5 Components and procedure as in Example 1, except that the quantity of methacrylic acid added amounts to 222g.

Example 7

Components and procedure as in Example 2, except that the quantity of methacrylic acid added amounts to 222 g.

10 Example 8

Components and procedure as in Example 3, except that the quantity of methacrylic acid added amounts to 222 g.

Example 9

- 15 Components and procedure as in Example 4, except that the quantity of methacrylic acid added amounts to 222 g.

Example 10

- 20 Components and procedure as in Example 5, except that the quantity of methacrylic acid added amounts to 222 g.

Example 11

- 25 Components and procedure as in Example 1, except that the acrylonitrile is replaced by methacrylonitrile.

Example 12

Components and procedure as in Example 1, except that the acrylonitrile is replaced by methylene glutarodinitrile.

30 Example 13

- The following components are introduced into a 40-litre capacity autoclave equipped with a stirring mechanism, a thermometer and inlets, and which is connected to a cooling system: 4.0 litres of desalted water, 4.0 litres of a 50% aqueous solution of the sodium salt of a diisobutyl naphthalene sulphonic acid, 250 g. of a mixture of sodium alkyl sulphonates with an average of 14 carbon atoms in the alkyl group and 222 g. of a 90% pure methacrylic acid. The entire aqueous phase is adjusted to pH 2.5 with dilute sulphuric acid. A solution containing 600 g. of a mixture of long-chain fatty acids with 12 to 18 carbon atoms in solution in 3,150 g. of acrylonitrile is then added. 8 g. of diisopropyl xanthogen disulphide are then added and the reaction vessel is rinsed with nitrogen. 6,250 g. of butadiene are then introduced under pressure and the contents of the autoclave are heated to 30°C.

- Polymerisation is initiated with a catalyst system containing the following components: 2 g. of potassium persulphate, 10 g. of the sodium salt of an alkyl sulphonic acid with an average of 14 carbon atoms in

the alkyl radical and 400 g. of water as the solvent.

Samples are taken at 30 minute intervals and their emulsified polymer content is determined by coagulating the latex with methanol and measuring the quantity of polymer. When the latex has a solids content of between 10 and 30%, a solution is added thereto in which 30 g. of diisopropyl xanthogen disulphide in 200 g. of acrylonitrile are dissolved. The above mentioned catalyst solution is then added. At a latex concentration of 20%, an emulsion containing the following components is added: 400 g. of a 5% aqueous solution of the sodium salt of diisobutyl naphthalene sulphonic acid, 3 g. of potassium persulphate and 15 g. of the sodium salt of an alkyl sulphonic acid with an average of 14 carbon atoms in the alkyl radical. After the latex concentration has reached a level of 40%, polymerisation is terminated as in Example 1 and the mixture is further processed. 21 kg. of an approximately 38% latex are obtained. It may either be used as a thin latex or creamed with sodium alginate.

Example 14

Procedure and components as in Example 7, except that acrylonitrile is replaced by an equivalent quantity of styrene. Approximately 27 kg. of an approximately 30% latex are obtained.

Example 15

Procedure and components as in Example 13, except that acrylonitrile is replaced by an equivalent quantity of styrene. About 21 kg. of an approximately 38% latex are obtained.

WHAT WE CLAIM IS:—

1. A copolymer latex containing in emulsified form a copolymer of from 40 to 98 parts by weight of a conjugated diene, 0.1 to 50 parts by weight of at least one monoolefinically unsaturated comonomer, 0.1 to 10 parts by weight of an olefinically unsaturated carboxylic acid having 3 to 6 carbon atoms and 0.1 to 10 parts by weight of a long chain carboxylic acid having 10 to 30 carbon atoms or a mixture of such acids.

2. A copolymer latex as claimed in claim 1 wherein the conjugated diene is butadiene, isoprene or chloroprene.

3. A copolymer latex as claimed in claim 1 or 2 wherein the monoolefinically unsaturated monomer is acrylonitrile, methacrylonitrile, ethyl acrylate, methyl methacrylate, vinyl acetate, vinyl chloride, styrene or α -methylstyrene.

4. A copolymer latex as claimed in any of claims 1 to 3 wherein the olefinically unsaturated carboxylic acid is acrylic acid or methacrylic acid.

5. A copolymer latex as claimed in any of claims 1 to 4 wherein the long chain carboxylic acid is a mixture of C_{12} to C_{14} aliphatic carboxylic acids.
- 5 6. A process for producing a copolymer latex which comprises emulsifying a mixture of (a) 40 to 98 parts by weight of a conjugated diene, (b) 0.1 to 50 parts by weight of at least one monoolefinically unsaturated comonomer, (c) 0.1 to 10 parts by weight of an olefinically unsaturated carboxylic acid having 3 to 6 carbon atoms and (d) 0.1 to 10 parts by weight of a long chain carboxylic acid having 10 to 30 carbon atoms 10 in an aqueous medium at a pH below 7, and polymerising the mixture in the presence of a free radical-forming catalyst and an emulsifier at a temperature in the range of from 5 to 100°C.
- 15 7. A process according to claim 6, wherein the conjugated diene is butadiene, isoprene or chloroprene.
- 20 8. A process according to claim 6, wherein the monoolefinically unsaturated monomer is acrylonitrile, methacrylonitrile, ethyl acrylate, methyl methacrylate, vinyl acetate, vinyl chloride, styrene or α -methylstyrene.
- 25 9. A process according to claim 6, wherein the olefinically unsaturated carboxylic acid is acrylic acid or methacrylic acid. 30
10. A process according to claim 6, wherein the long chain carboxylic acid is a mixture of C_{12} to C_{14} aliphatic carboxylic acids. 35
11. A process according to claim 6, wherein the emulsifying is effected by means of an anionic emulsifier.
12. In a method of producing shaped articles by dipping a mould first into a bath containing a coagulation solution, and subsequently into a polymer latex to form a polymer film on the mould, the improvement which comprises carrying out this process with the latex of claim 1 as the polymer latex. 40 45
13. A shaped article produced according to the improved method of claim 12.
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